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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the production of Olefins

5 We, COMPAGNIE FRANCAISE DE RAFFINAGE, a French Body Corporate of 5, rue Michel Ange, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the conversion of high-molecular aliphatic saturated hydrocarbons, pure or in mixture, into mixtures rich in lower-molecular olefins, the conversion being carried out by reaction in the vapour phase in the presence of small quantities of oxygen. The process according to the invention is applied more particularly to straight-chain 15 aliphatic saturated hydrocarbons containing between 12 and 40 carbon atoms per molecule.

20 There is an increasing demand for olefins having 10 to 20 carbon atoms in a straight chain and with an α double bond. These olefins are used for the manufacture of alkyl-benzenesulphonates with a straight-chain alkyl radical, and such products are at present required as biodegradable detergents, i.e., 25 detergents which are destructible by the action of micro-organisms in effluents. α double bond olefins are also used in the synthesis of numerous organic products, more particularly alcohols by oxo synthesis.

30 It is therefore very important that there should be an economic process for the production of long-chain α olefins.

35 Various means have already been proposed for the production of such olefins, *inter alia* the polymerisation of ethylene on a catalyst of the Ziegler type. The main process for the production of straight-chain olefins has, however, been by the cracking of paraffins.

40 Thermal or steam cracking processes have been the most frequently used heretofore, catalytic cracking tending to result in isomerisation reactions together with chain-breaking reactions.

45 For example, it is possible to obtain long-chain straight olefins by cracking a solid paraffin formed mainly from straight-chain [Price 4s. 6d.]

aliphatic saturated hydrocarbons in the presence of water vapour at a temperature of from 500—650° C with a reaction time of several seconds, but thermal cracking gives 50 relatively appreciable quantities of low-molecular olefins, more particularly ethylene, to the detriment of olefins having more than 5 carbon atoms. Also, a carbon deposit forms in the reactor and this tends to reduce the 55 reaction speed.

It is also possible to obtain rates of conversion equivalent to those obtained in thermal cracking alone, with a very much shorter contact time, if the operation is carried out in the presence of small quantities of oxygen 60 which acts as a reaction initiator. Olefin hydrocarbons of low-molecular weight have already been produced in this way, more particularly ethylene and propylene, from straight-chain 65 paraffin hydrocarbons having from 2—7 carbon atoms. Olefins having from 10—20 carbon atoms can also be obtained by oxidation cracking of paraffin hydrocarbons having a high content of straight-chain paraffins, provided 70 that the heat produced by the exothermic reaction is carried off and also provided that the heat produced by the exothermic reaction is carried off and also provided that the oxygen-hydrocarbon mixture used is 75 sufficiently homogeneous to prevent the places where there is an excessive oxygen concentration from becoming the site of combustion reactions pure and simple with the formation of carbon dioxide and water. Heretofore, the 80 heat was carried off and the mixture was made homogeneous by a complicated process comprising introduction of oxygen through a plurality of side inlets and by the dropping of a shower of inert solid particles in counter-current with the gas mixture. 85

The disadvantage of this process is that it results in an appreciable inert surface inside the reactor. It is well known that any increase in the surface results in a reduction of the 90 speed of the oxidation cracking reactions. The presence of such particles therefore makes it

necessary to increase the contact time and the reactor volume for a given conversion rate. Also, cooling and recirculation of these particles requires expensive apparatus which is difficult to use.

The object of the invention is to provide a long-chain olefin production process to obviate these disadvantages and which is much simpler to apply.

The process according to the invention is a selective process for the production of straight-chain olefins having from 10—20 carbon atoms with an α double bond.

The invention relates to a cracking reaction for saturated hydrocarbons in the presence of small quantities of oxygen, such reaction being characterised in that the reaction time is between 0.02 and 1 second, preferably between 0.1 and 0.5 second and the reactor used has no filling whatever, an elevated temperature being maintained therein and the oxidising gas and the hydrocarbon being introduced into the reactor in one operation at a temperature below the temperature in the reactor in the form of a very homogeneous mixture.

Research by Applicants shows that if the oxidising gas and the hydrocarbon for cracking are mixed in one operation in a narrow tube for a sufficiently short period after having been separately preheated, the temperature increase in the reactor as a result of the exothermic reaction depends only on the reaction temperature, the oxygen-hydrocarbon weight ratio and the space velocity of the gas mixture; the gas mixture is very homogeneous and this results in a very small number of combustion reactions in the reactor; the effluent contains only small quantities of CO_2 , the CO_2/CO ratio being, for example, equal to 1/10; also, only a small amount of oxygenated products forms; a very short reaction time promotes the formation of olefins at the expense of oxygenated products; the olefins forming during the reaction are straight-chain olefins and the majority of them—approximately 90%—have an α double bond.

The process according to the invention therefore comprises:

Separate preheating of the hydrocarbon charge for cracking and the oxidising gas to a temperature 20—150° C below the temperature in the reactor so that the temperature increase due to the reaction heat makes up for this difference.

Mixing the resultant two currents of gas in a very short time in a zone in which the surface/volume ratio is large, for example in a small section tube, so as to give a turbulent flow which promotes the mixing and slows down the reaction advance by surface effect;

Introduction of the resultant mixture into the reaction zone at a rate such that the retention time of the gases is between 0.02 and 1 second, preferably between 0.1 and 0.5 second;

Quenching of the reaction effluent to a temperature of about 200—250° C, at which the olefins which are formed no longer react with the oxygen, such quenching being carried out by any known means, for example by injection of a cold fluid, such as water vapour.

In performance of the invention, the charge may be a pure n-paraffin hydrocarbon (i.e. a straight-chain saturated aliphatic hydrocarbon), having at least 10 carbon atom, preferably 12 to 40 carbon atoms, a n-paraffin hydrocarbon mixture, or mixtures containing a high proportion of n-paraffin hydrocarbons, such as mixtures constituting gas oils, crude paraffins and the petrolatum resulting from the dewaxing of oils. Vaporisation of the heaviest charges is preferably carried out in the presence of water vapour.

The oxidising gas may be pure oxygen although it is preferable to use oxygen diluted in an inert gas. To this end, air is used for preference, since it avoids any risk of explosive reactions in the event of malfunctioning of the apparatus. The air is also used as a diluent for the hydrocarbon vapours when water vapour is not used and thus forms a vehicle for elimination of the reaction heat.

Unlike the mixing zone, the reactor must have the smallest possible surface/volume ratio and hence the coil form will be avoided. Research carried out by Applicants shows that to homogenise the temperature in the reactor the gases must be introduced into the reactor tangentially to one of its walls.

The reaction temperature must be between 500°C and 750°C. Below 500°C oxygenated products form at the expense of the olefins and the reaction speed is too low, while above 750°C there is appreciable combustion of the charge with the formation of CO_2 and water. For paraffin hydrocarbons containing approximately 16 carbon atoms per molecule this reaction temperature must be between 575 and 650°C.

Although the pressure used can vary slightly and be above or below atmospheric pressure it is preferable, according to the invention, to use a pressure substantially the same as atmospheric pressure.

The oxygen/hydrocarbon ratio by weight is between 0.014/1 and 0.23/1. Preferably, an oxygen/hydrocarbon ratio by weight of between 0.031/1 and 0.07/1 is used for the reaction. If the ratio used is below 0.014/1 the reaction is not quick enough and if it is above 0.23/1 the hydrocarbon consumption due to the formation of carbon monoxide becomes appreciable.

The reaction time is calculated from the time when the mixture of gases enters the reactor, i.e., the time when they have acquired the required temperature conditions for the reaction. Applicants have found that although a reaction time of more than 1 second gives a higher rate of conversion it results in the

formation of oxygenated products at the expense of the required olefins.

- 5 In addition to the portion of charge which has not reacted, a mixture of various oxygenated products and olefins containing a varying number of carbon atoms is obtained after quenching.

- 10 If, for example, pure n-hexadecane is used as a charge, the unreacted charge fraction is readily separated by distillation and in addition to n-hexadecane it contains a small proportion of oxygenated products, more particularly of the epoxy type, in C/16.

- 15 The distilled products containing the required olefins contain about 20% of oxygenated products. These compounds comprise approximately 50% of carbonyl function substances and 50% ether type substances.

- 20 For exploitation these compounds can be separated by various means, for example by distillation or by preferential dissolution in selective solvents, or by combination with reagents, such as sodium bisulphite.

- 25 According to the invention, all the oxygenated products and/or the hydrocarbons having a higher boiling point than that of the required products can be recycled in the feed charge together with the unreacted fraction. Research by Applicants has shown that the oxygenated products can not only be converted into useful products but also increase the speed of conversion of the feed charge.

- 30 The above-described process has numerous advantages;

- 35 The small surface of the reactor in relation to its volume and the high reaction temperature greatly reduces the retention time of the gas in the reactor and hence a considerable quantity of gas can be treated in a relatively small apparatus.

- 40 The relatively high reaction temperature and the homogeneous mixture of oxidising gas and hydrocarbon for cracking enable heat elimination problems to be reduced simply to control of the temperature of the mixture of gases at the reactor inlet.

- 45 The quantities of light olefins below C₂ obtained are relatively small in relation to the quantities of heavier olefins.

- 50 Any danger of carbon deposit is completely eliminated and the reactor remains quite clean.

- 55 The oxygenated products forming during the resolution represent only a small quantity and therefore do not affect subsequent use of the olefins produced.

The aldehydes and ketones containing more than 5 carbon atoms produced by this process are products which were hitherto prepared by oxo synthesis.

The invention is illustrated by the following Examples. These Examples have no limiting force and the invention is applied to any of the above products and mixtures of products as charges in the performance of the process.

60 In the Examples, the oxygen and hydrocarbons are preheated separately to a temperature of about 100°C below the reaction temperature and are then mixed in a mixing zone which is upstream of the reactor and formed by narrow piping, the mixing being performed in a time which is about 6% of the reaction time. The mixed gases are then introduced into the reactor through one inlet, tangentially to the wall of the reactor.

EXAMPLE 1

75 A rate of flow of 704 cc/h of 95% n-hexadecane and 116 litres/h of air is maintained in a cylindrical reactor 2.7 cm in diameter and 14 cc in volume so as to give a vapour retention time of 0.1 second in the reactor, the latter being at a temperature of 575°C.

80 The results of this test are shown in the first column of Table 1.

EXAMPLE 2

85 A rate of flow of 323 cc/h of n-hexadecane and 53.3 l/h of air is maintained in the same reactor, the latter being at a temperature of 650°C, and this corresponds to a contact time of 0.2 seconds.

90 The results are given in column 2 in Table 1.

EXAMPLE 3

95 Under the same conditions as in Example 2 the reactor is fed with 194 cc/h of n-hexadecane and 16 l/h of air, corresponding to a contact time of 0.4 seconds.

The results are given in column 3 in Table 1.

EXAMPLE 4

100 In a 32.8 cc reactor a current of n-hexadecane is maintained at 82.5 cc/h and a rate of flow of 13.6 l/h of air, corresponding to a gas retention time in the reactor of 2 seconds. The temperature in the reactor is kept at 575°C.

105 The results are shown in column 4 of Table I.

TABLE I

Examples		1	2	3	4
Operating conditions;					
Temperature °C		575	650	650	575
Oxygen/n-hexadecane molar ratio		0.4	0.4	0.2	0.4
Retention time in reactor, in seconds		0.1	0.2	0.5	2
Conversion: Hydrocarbon	%	26.2	38.2	34.0	41.9
	Oxygen %	77.6	88.2	85.7	95.4
Yield in % by weight of converted hydrocarbon:					
C ₂ H		11.5	14.2	11.2	11.7
C ₃ H ₆		7.5	8.2	6.5	5.2
C ₄ H ₈		6.2	6.3	5.7	4.0
Olefins ≥ C ₅		53.8	52.0	52.0	40.5
Organic oxygenated products		20.6	15.0	13.7	31.9
H ₂ O		11.4	6.9	3.2	7.2
CO		2.5	2.9	3.7	3.5
CO ₂		traces	traces	traces	traces

Comparison of the above examples gives the following conclusions:

- 5 For a given oxygen-hydrocarbon molar ratio a longer contact times results in the formation of a much greater quantity of oxygenated products during the reaction.

- 10 31.9% of oxygenated products are obtained in fact in Example 4 while only 15% are obtained in Example 2 for substantially equal quantities of oxygen used.

- 15 A longer contact time with a smaller quantity of oxygen used gives a lower conversion rate for substantially the same distribution of products. In Examples 2 and 3 there are 52% of olefins greater than C₄ in the cracked products and about 15% of oxygenated products.

- 20 To limit the amount of oxygenated products forming while maintaining a good conversion rate for the charge the contact times must therefore be less than 1 second and even less than or equal to 0.5 second.

EXAMPLE 5

This Example shows the advantage of recycling in the feed charge—the oxidised products and/or hydrocarbons having a boiling point above that of the required olefins. 25

The results obtained are shown in Table II.

In a first test (Test L 13) the charge is n-hexadecane alone. From the reaction products there are separated and store without recycling: the unconverted n-C 16 and the heavy oxidised products, i.e., the products having a boiling point above that of the required olefins. 30 35

In a second pass (Test L 20) the charge is formed partly from the stock of previously collected products together with the fresh charge. The unconverted n-hexadecane and the heavy oxidised products are again separated from the reaction products and collected. In a third pass (Test L 21) the products for recycling from the preceding test are incorporated in the charge, and so on. 40 45

TABLE II
Common operating conditions: Temperature = 650°C.
Retention time = 0.2 sec.

Test Designation	L.13	L.20	L.21
Liquid feed charge in grams			
Fresh n-hexadecane	100	36.9	42.6
Recycle { n-hexadecane	0	58.3	50.9
{ heavy oxidised products	0	4.8	6.5
	100.—	100.—	100.—
Feed oxygen, in grams	5.7	5.8	5.6
Products formed, by weight per 100g of liquid feed			
a) Hydrogen and saturated gases	2.7	3.3	3.4
Olefins and diolefins O_2 , C_2 , C_4	11.1	13.8	16.6
Straight-chain olefins $C \geq 5$	20.1	22.4	24.1
H_2O	2.7	2.7	2.5
CO (+ traces of CO_2)	1.2	1.4	1.9
Light oxidised products	4.0	4.6	5.1
b) Recyclable products			
{ n C 16 unconverted	58.3	50.9	45.0
{ heavy oxidised products	4.8	6.5	5.1
Conversion per pass in g per 100 g of liquid charge n C 16	41.7	44.3	48.5
Yield in g per 100 of converted n C 16 α linear olefins $C > 5$	43.5	44.9	45.6

It has been found that recycling in this form does not increase the quantity of heavy oxidised products collected, and this proves that they are converted as they form; and increases the conversion per pass of the feed charge

without reducing the $C \geq 5$ linear olefin yield per 100 g of converted n C 16.

The following Table shows the distribution in percentage by weight of the olefins and oxidised products obtained in Example 5.

Number of atoms of carbon per molecule.	Olefine in a straight chain in % of the fraction C5—C15.		
	Test L 13	Test L 20	Test L 21
Weight of olefins straight chain > C5 per 100 grams of charge	20.1	22.1	24.1
C 5	11.09	11.97	12.04
6	15.73	16.24	16.20
7	10.83	10.55	10.14
8	8.91	9.14	8.33
9	9.39	8.99	8.63
10	9.39	8.54	8.74
11	8.43	7.39	8.37
12	8.43	8.19	7.24
13	7.94	6.98	7.51
14	7.04	7.14	7.82
15	2.82	4.87	4.98

This Table shows that the olefins having at least 10 atoms of carbon per molecule represent 44.05, 43.11 and 44.66% by weight of the olefins whose number of carbon atoms is equal to or greater than 5.

EXAMPLES 6 AND 7.

These examples illustrate the treatment of mixtures of petroleum hydrocarbons containing a high proportion of n-paraffin hydrocarbon.

The apparatus used is as defined in Example 1. A small quantity of nitrogen or water vapour is admitted during the preheating of the hydrocarbon charge to facilitate vaporisation.

In Example 6, the paraffin treated was a white crystallised refined wax having a mean

molecular weight of 350 and containing approximately 90% of straight-chain constituents. The conditions used are as shown in Table III, at 700°C (Column 1) and at 600°C (Column 2). The degree of conversion and the yields of the products obtained per 100 g of converted starting products are respectively given in each column.

In Example 7, a crude oil-free wax was treated, having been obtained from the dewaxing of lubricating oils and having a mean molecular weight of 422 and containing approximately 80% of straight-chain constituents.

The treatment conditions and the results are shown in Table III (Column 3).

TABLE III

Example No.		(6)	(7)
Charge for treatment		Refined wax	oil-free crude wax
Operating conditions	Temperature °C	700	650
	Molar ratio O ₂ /HC	0.41	0.0
	Ratio by weight O ₂ /HC	0.0375	0.0365
	Volume (liquid)/Vol. Hour	32.9	35.9
	Retention time sec.	0.20	0.20
Conversions	Hydrocarbon	43.3	34.0
	Oxygen	95.3	96.1
Products formed per 100 g of converted products	Saturated hydrocarbons	6.2	5.6
	C ₂ H ₆	13.7	8.7
	C ₃ H ₈	5.1	5.6
	C ₄ H ₁₀	4.3	4.1
	Olefins C ₅ to C ₂₀	51.9	59.5
	Organic oxidised products	19.4	19.2
	H ₂ O	3.5	4.4
	CO	1.9	1.9

WHAT WE CLAIM IS:—

1. A cracking process of an n-paraffinic feedstock in the presence of oxygen or of an oxygen containing gas to manufacture olefins, a substantial part of which being straight-chain α olefins with more than 10 carbon atoms per molecule, wherein the reaction time is between 0.02 and 1 second, the temperature is between 500 and 750°C, the oxygen to hydrocarbon weight ratio is between 0.014/1 and 0.23/1, and the mixture of oxidizing gas and hydrocarbon preheated to a temperature of 20—150°C less than that of the reaction zone is introduced through one inlet, tangentially to the wall of the reactor which contains no solids prior to use.
2. A process as claimed in claim 1, wherein said n-paraffin contains from 12 to 40 carbon atoms.
3. A process as claimed in claim 1 or claim 2, wherein the oxygen-containing gas and the charge for cracking are introduced into the

reactor at a temperature from 20—150°C below the temperature in the reactor.

4. A process as claimed in any preceding claim, wherein the temperature in the reaction zone is kept between 575 and 650°C.

5. A process as claimed in any preceding claim, wherein the oxygen-hydrocarbon weight ratio is between 0.03/1 and 0.07/1.

6. A process as claimed in any preceding claim, wherein the gas retention time under the reaction conditions is between 0.1 and 0.5 second.

7. A process as claimed in any preceding claim, wherein the reaction products are quenched to a temperature between 200 and 250°C.

8. A process according to any of the preceding claims wherein the oxidised products and the hydrocarbons having a boiling point above that of the required olefins are recycled in the charge for treatment.

9. Application of the process according to

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Claim 1 to the production of straight-chain α -olefin from n-hexadecane.

10. A process for the production of straight-chain olefins substantially as described herein with reference to the foregoing Examples.
- 5 11. Straight-chain olefins when prepared by the process of any of claims 1 to 10.

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